Tutorial on Upgrading of Oilsands Bitumen

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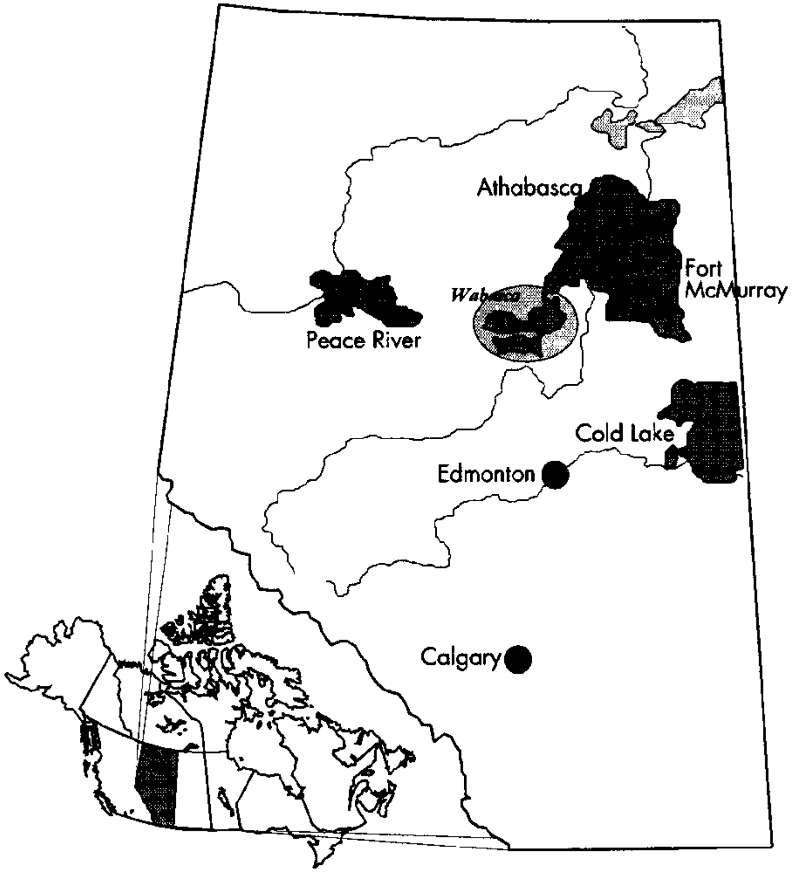
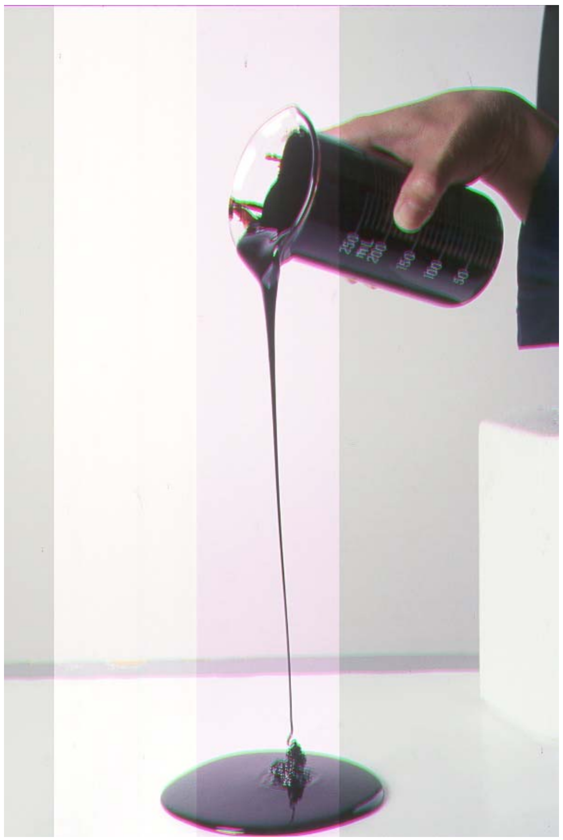
What is Oilsands Bitumen?

- Heavy crude oil extracted from oilsands
- High viscosity, high sulfur oils
- Major production from mining near Fort McMurray, Alberta
- Also produced at Cold Lake and Peace River



Why Upgrade Bitumen?



- Oil refineries are designed for lighter crudes (density < 950 kg/m^3)
- Bitumen has density over 1000 kg/m^3, over 4% sulfur, viscosity 1000x light crude oil
- Needs upgrading to sell to most refineries

Bitumen and Heavy Oil Upgrading

Upgrading: any fractionation or chemical treatment of bitumen or heavy oil to increase its value

- Minimum objective: reduce the viscosity to allow shipment by pipeline without adding a solvent
- Maximum objective: process to give a crude oil substitute of high quality (a “synthetic crude oil”)

Bitumen and Heavy Oil Upgrading

- Minimum upgrading approach
  - Reduce viscosity and control solids and water
  - None in operation; research underway on simple, small scale processes
- Full upgrading approach
  - Reduce sulfur and maximize distillable oil
  - Large expensive plants much like refineries
- Focus on oil components that are too heavy to distill (boiling point over 524 °C)

Bitumen Properties

- Up to 1/2 of the bitumen can be recovered by distillation under a vacuum
- The residue contains large molecules, with molecular weights over 400
- Complex mixture of chemical species, including aromatics, substituted aromatics, organic sulfur and nitrogen compounds

Sulfur, Nitrogen and Metals in Residue Fraction of Feeds

	Sulfur, wt%	Nitrogen, wt%
Athabasca	5.14	0.56
Cold Lake	5.10	0.45
Lloydminster	4.69	0.53
Peace River	7.02	0.63

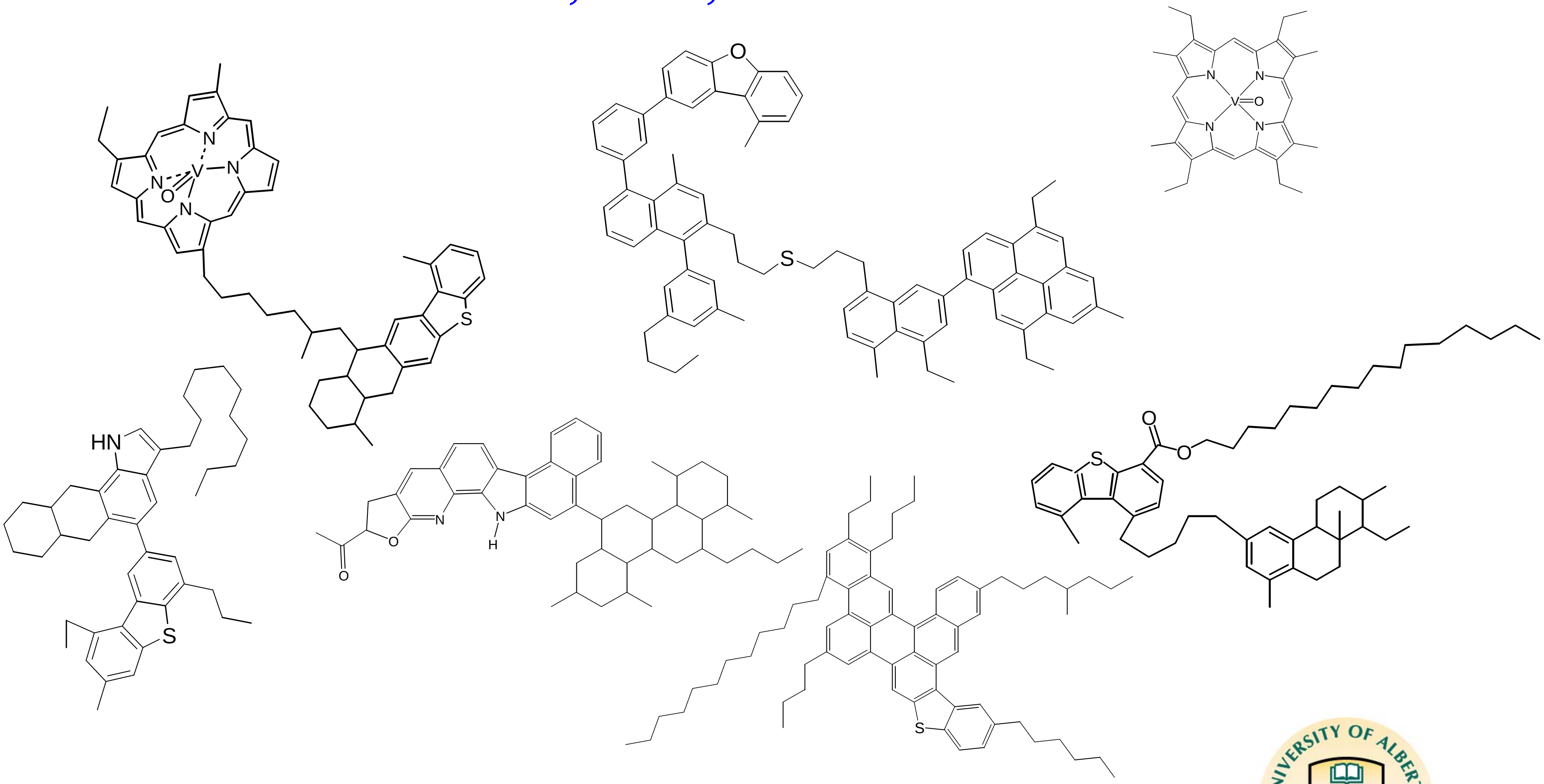
	Metals, ppm	
	Nickel	Vanadium
Athabasca	150	290
Cold Lake	200	490
Lloydminster	140	190
Peace River	130	410

Asphaltenes in Bitumen

- Dilution of Alberta bitumens in n-pentane or n-heptane gives 10-20% of brown/black solid precipitate
- This fraction is called “asphaltene”, contains highest molecular weight (up to 5000) and most polar components in the oil
- Asphaltenes are very reactive during processing

Asphaltene molecules

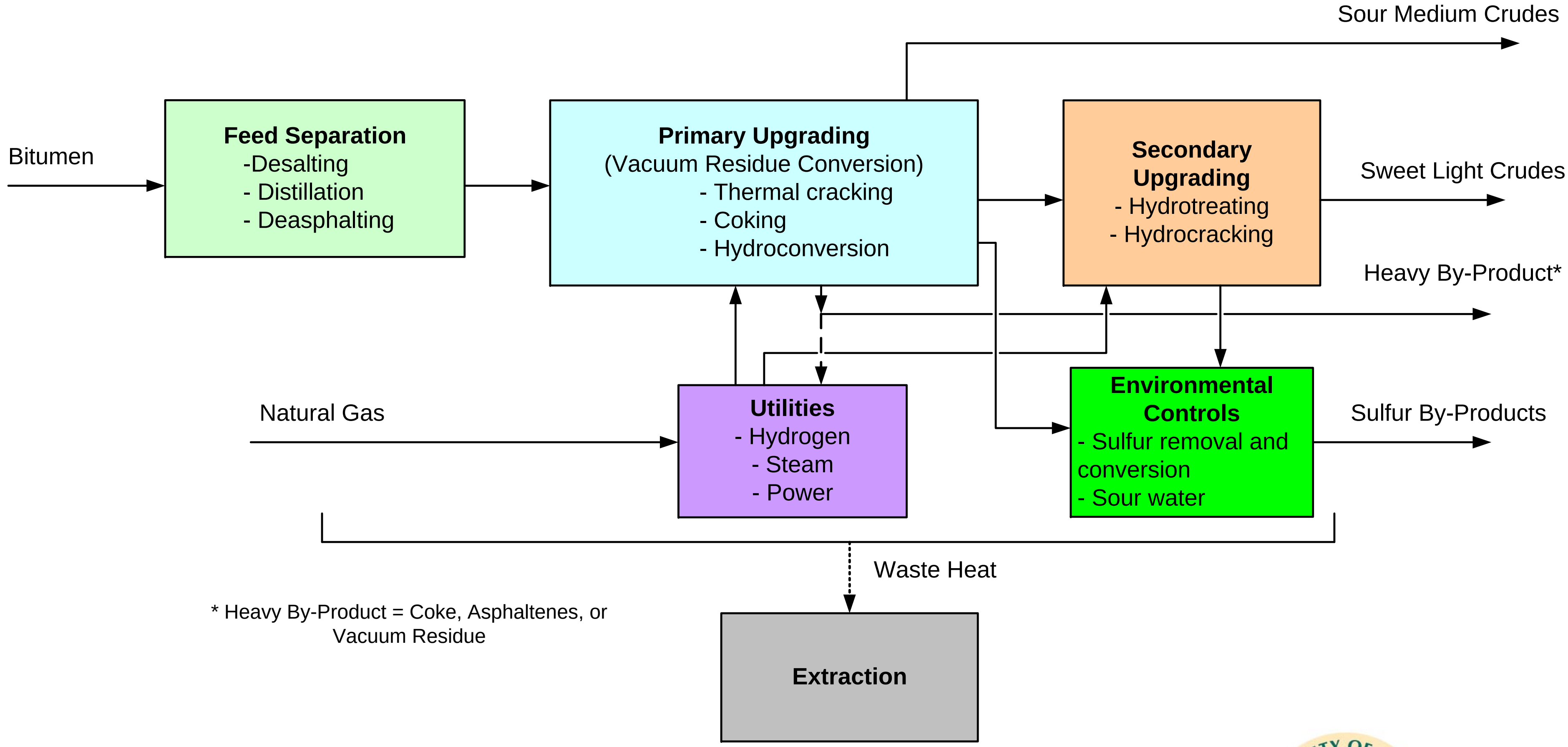
Based on Sheremata et al., 2004; Strausz 1999



Upgrading Steps

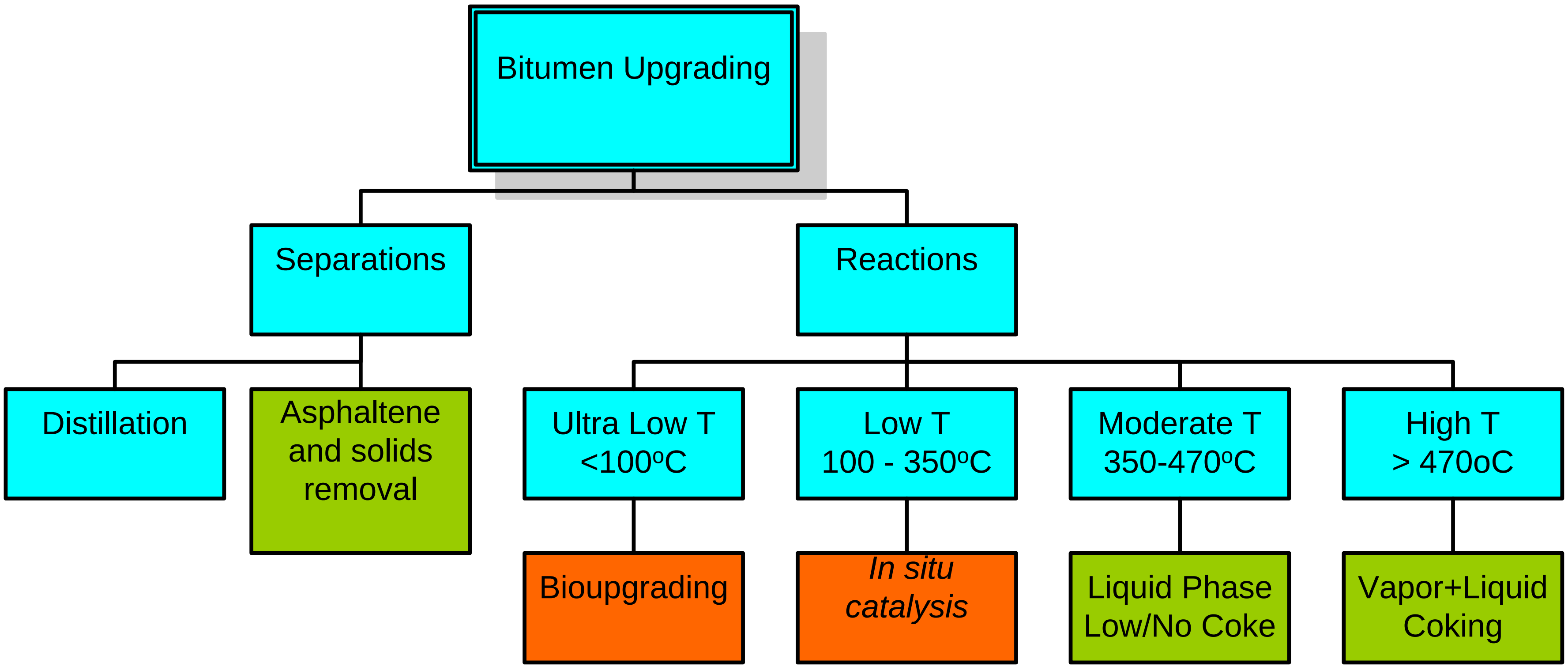
- Large molecules that will not distill (called "Residue") must be *cracked* to give lighter molecules
- Cracking takes place in the *primary upgrading* step at over 400 °C
- Cracking products rich in sulfur and nitrogen, so *secondary upgrading* is required to get sulfur below 0.5%

General Upgrading Scheme



* Heavy By-Product = Coke, Asphaltenes, or Vacuum Residue

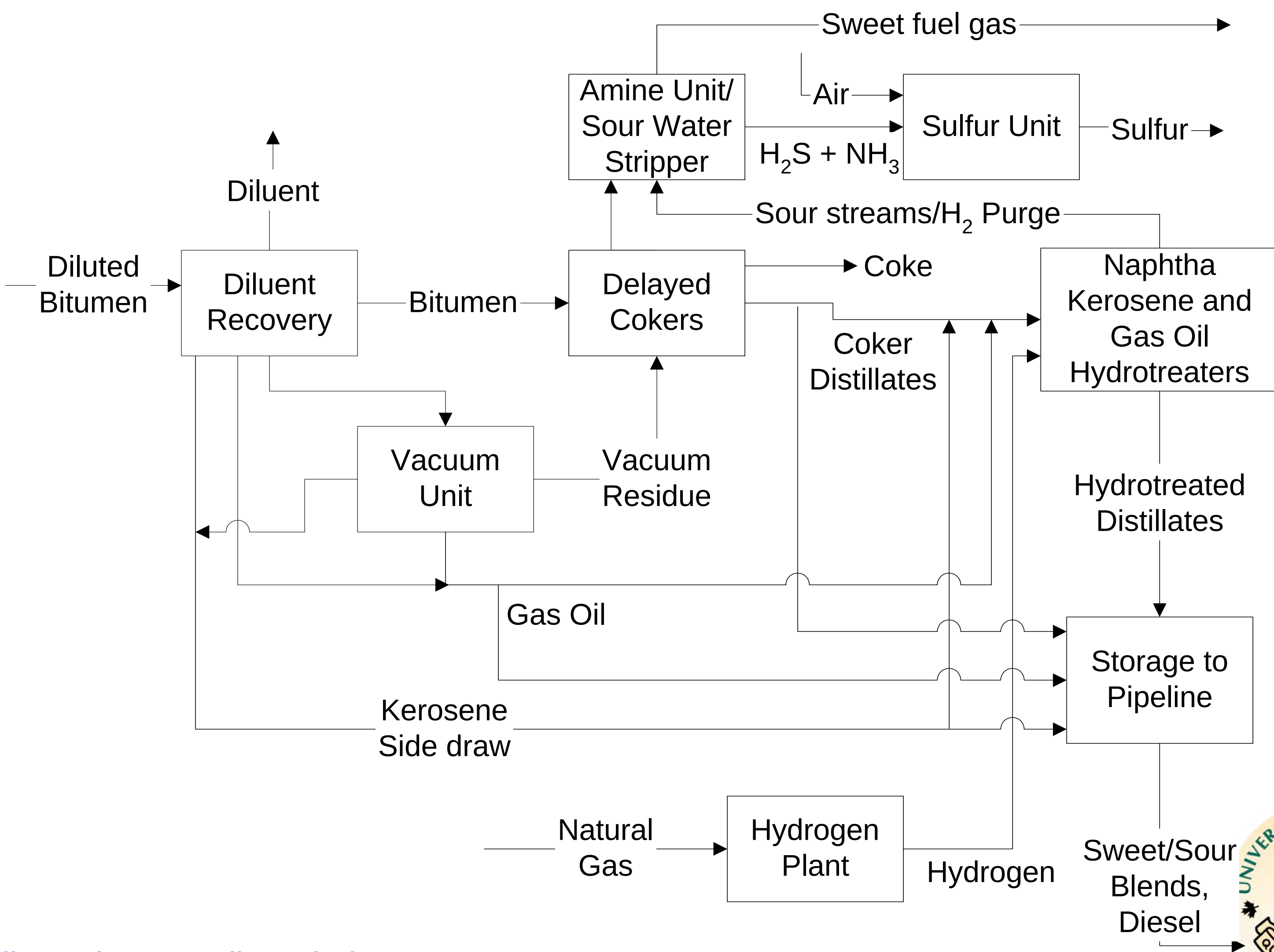
Upgrading Technologies



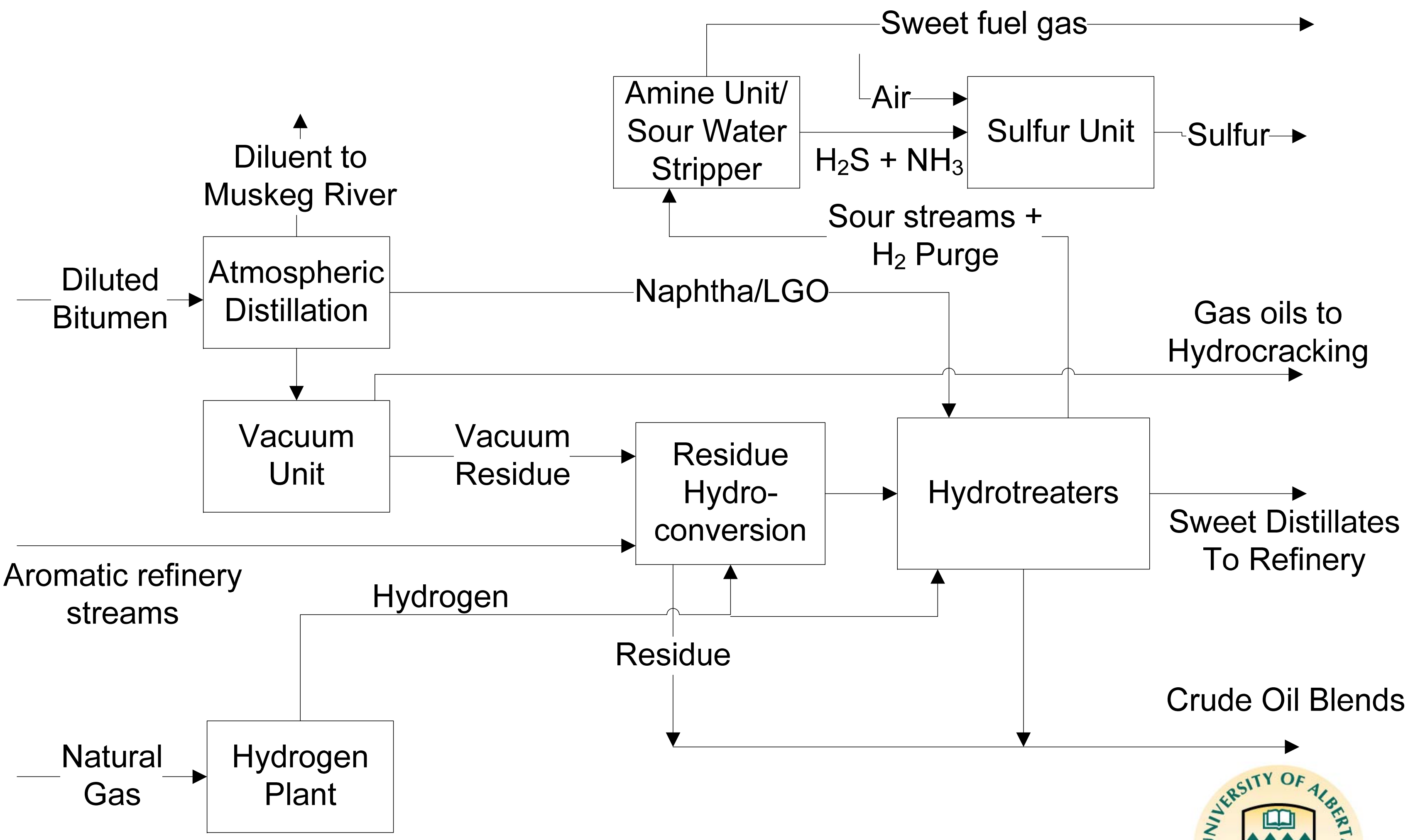
Commercial technology

Under development

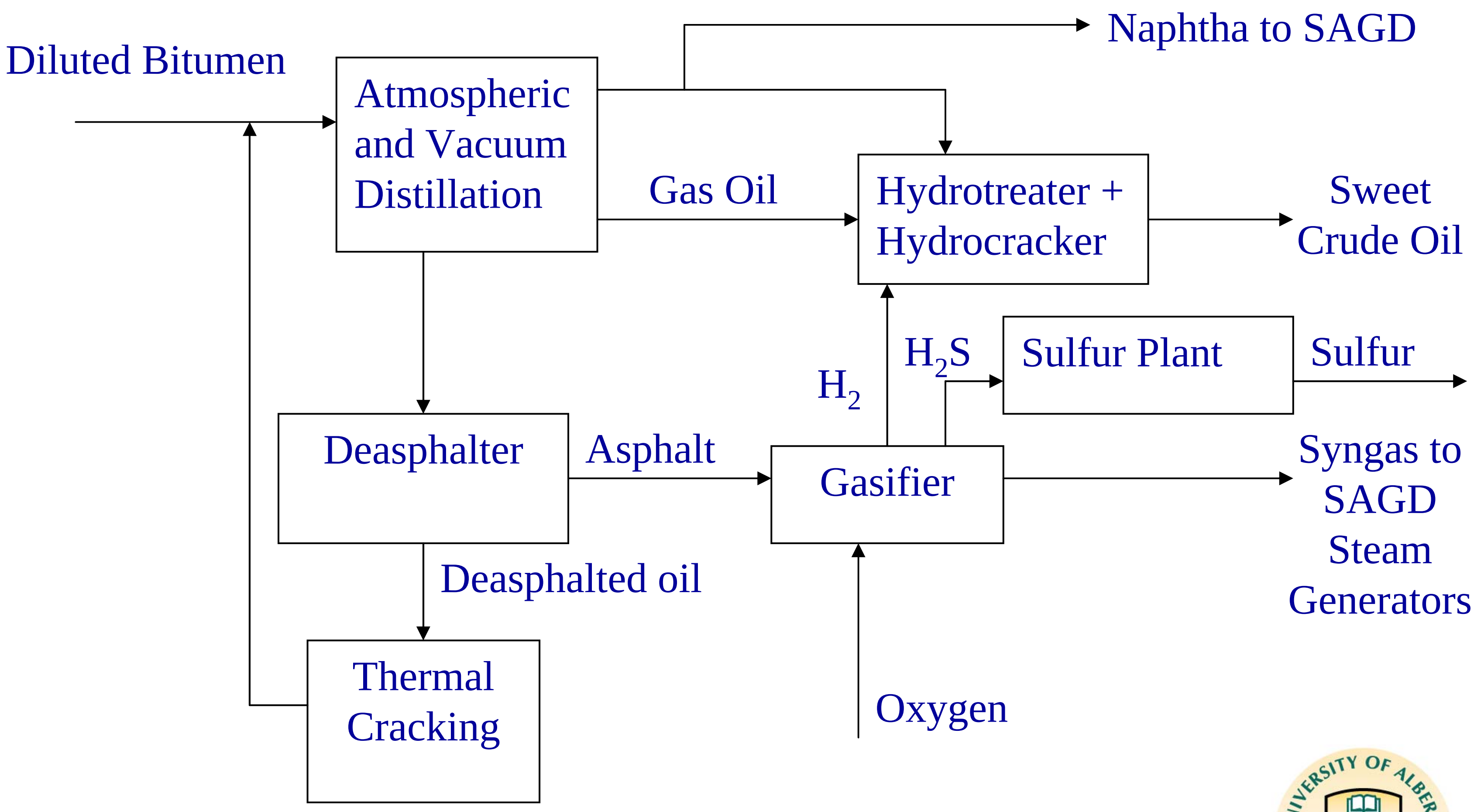
Suncor Base Plant and Millennium



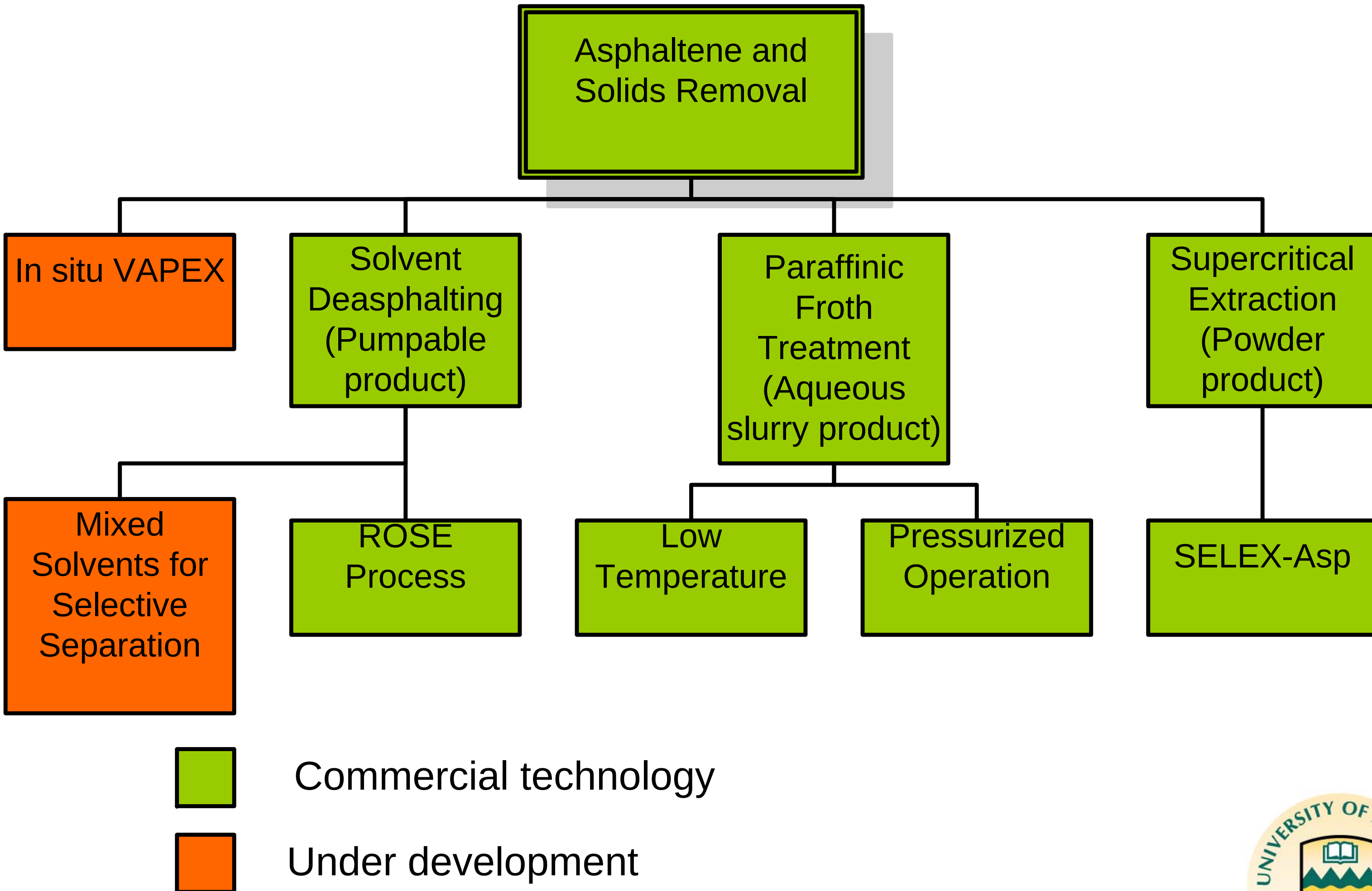
Shell Upgrader



Long Lake Upgrader



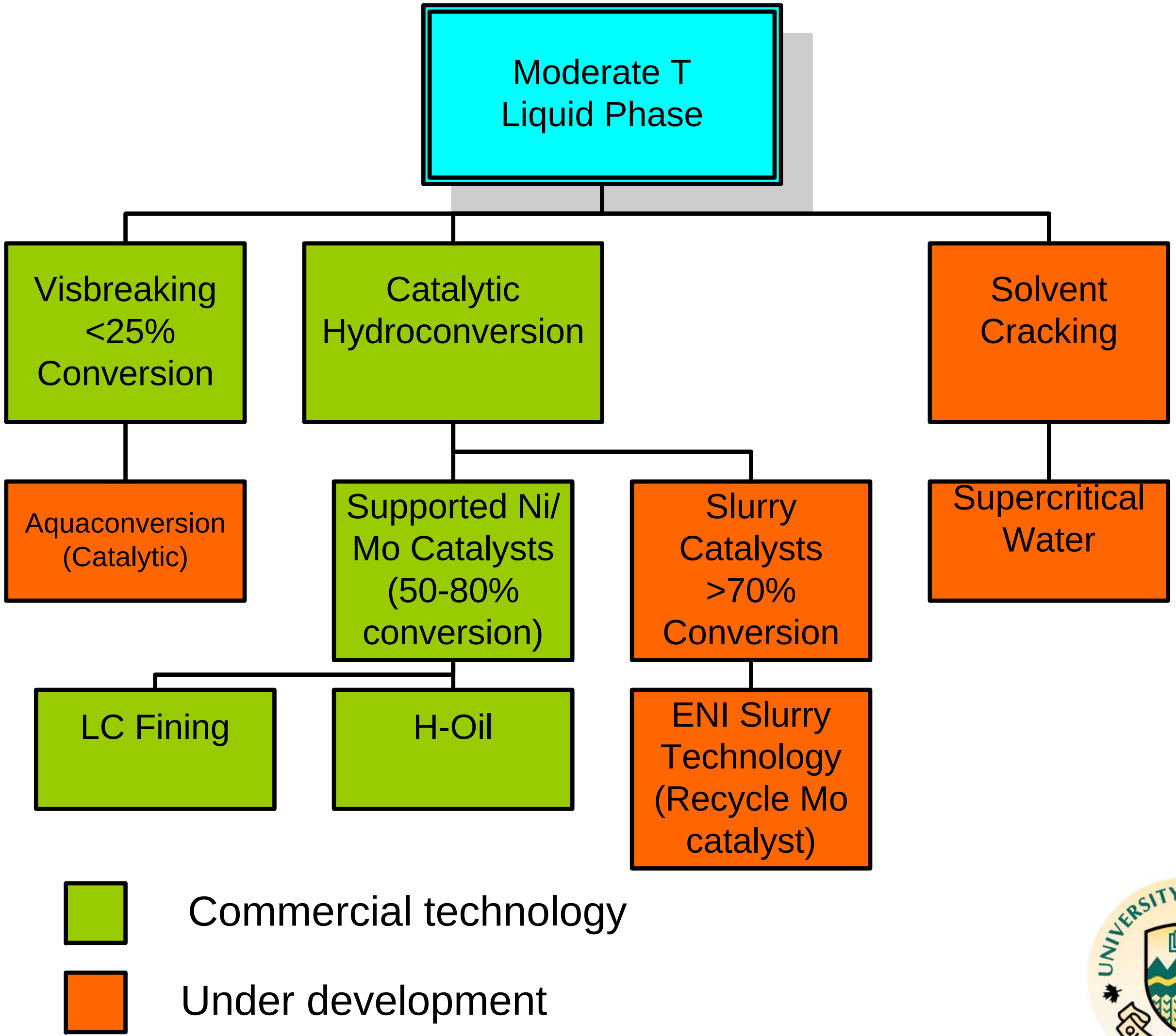
Asphaltene Separations



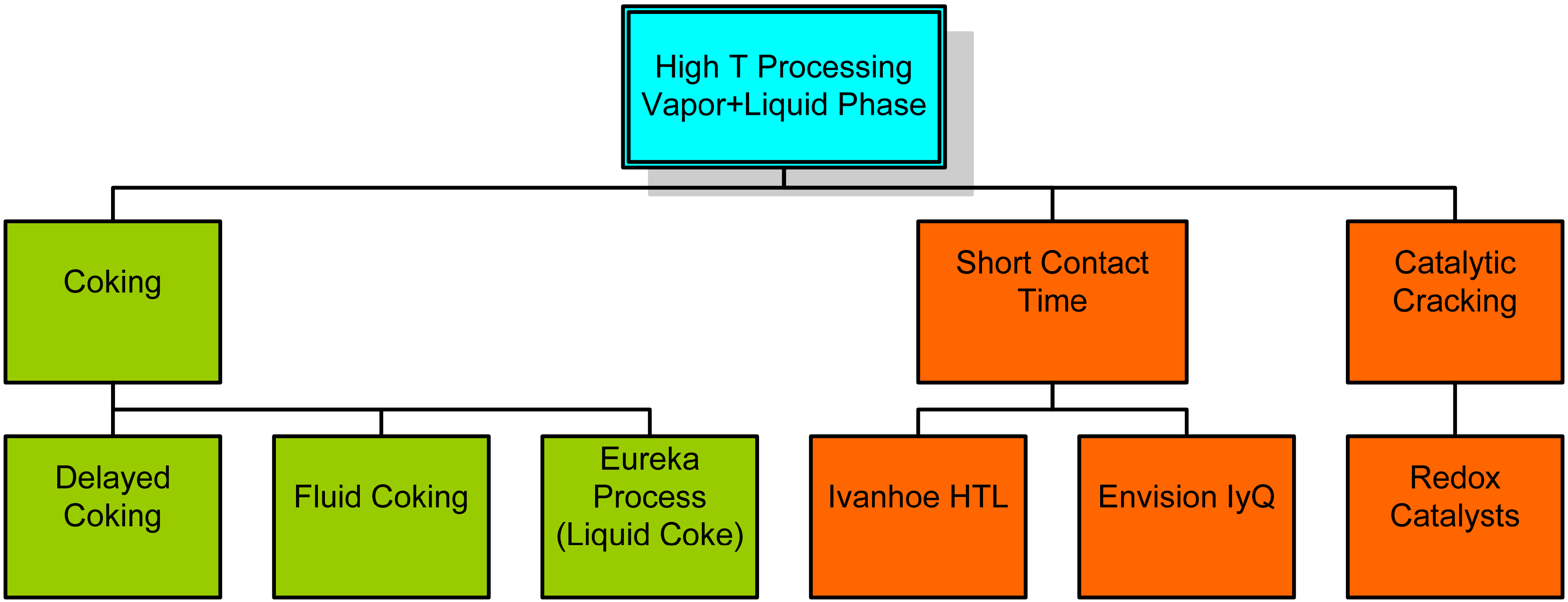
Solvent Deasphalting

- Precipitate asphaltenes using paraffinic solvents (propane to hexane; C_3-C_6)
- Solvent:oil ratio is 4:1 or higher - more solvent gives cleaner separation
- Major utility cost is solvent recovery
- Separation of oil and solvent is easy above T_c of solvent, minimizing energy costs
- Nexen Long Lake only oilsands example

Moderate Temperature Processes



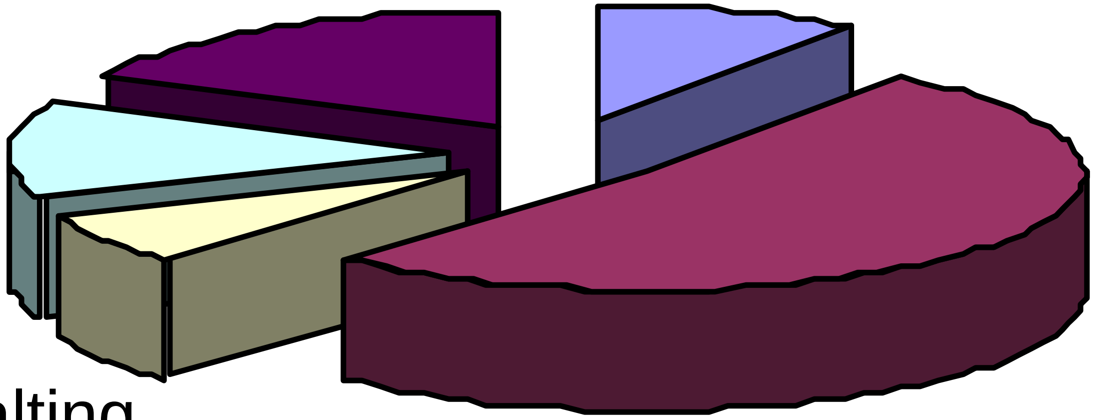
High Temperature Processes



Commercial technology

Under development

Processes for Primary Upgrading



North America + Venezuela, 1998

Thermal Conversion

- Thermal cracking underlies all current commercial reactor technology
- Rely on hydrogen gas to stabilize products

Process Characteristics - Coking

- Low pressure, reliable, safe process
- Low operating costs
- Low liquid product yields
- Coke by product is rich in sulfur, so this material is stockpiled in mines
- Main process for CNRL, Suncor and Syncrude

A Coke Primer

coke (kok) *noun*
A solid residue left after incomplete combustion of petroleum etc.

Probably from Northern English dialect
colk, core, of unknown origin

Thermal Cracking Reactions

- Breaking a C-C bonds required to get significant upgrading
- Two types of products - one stable and one unsaturated and unstable (alkenes)
- Use catalytic hydrotreating to stabilize the unsaturated products

Coking Technologies

- Delayed coking - liquid feed cracks in a large drum, and coke accumulates at the bottom with time (CNRL and Suncor)
- Fluid coking - liquid feed is sprayed into a bed of hot coke particles (Syncrude)

Hydrogen Addition Processes

- Hydroconversion or Hydroprocessing
  - Combine some catalytic activity with thermal cracking
- Hydrotreating
  - Catalytic sulfur and nitrogen removal
  - Minimal cracking
- Hydrocracking
  - Gasoline production using a bifunctional catalyst

Hydroconversion

- Used by Husky, Shell, and Syncrude for primary upgrading
- Feed cracks in the presence of hydrogen and a supported-metal catalyst (Mo + Ni on aluminum oxide)
- Hydrogen suppresses coke, helps remove sulfur

Hydrotreating

- Lower temperature process, with a similar catalyst (nickel + molybdenum on a support of aluminum oxide)
- High level (>90%) removal of sulfur, >70% removal of nitrogen
- Negligible cracking

Hydrocracking

- High pressure catalytic process used by refineries (Shell Scotford, Suncor Edmonton) to convert heavy distillates into feeds for gasoline
- Catalyst gives both cracking (e.g. zeolite) and hydrogenation activity
- Higher hydrogen pressure than hydroconversion or hydrotreating